



Le 2^{ème} Séminaire International sur les Energies Nouvelles et
Renouvelables
The 2nd International Seminar on New and Renewable
Energies

Unité de Recherche Appliquée en Energies Renouvelables,
Ghardaïa – Algérie 15, 16 et 17 Octobre 2012



Methanol as a clean renewable fuel

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Abstract— Oxygenated hydrocarbons play an important role as fuels in combustion, as well as in industrial processes and environmental chemistry. Methanol, which is the simplest alcohol, is a clean renewable fuel with a large part of useful energy and is in great demand as an intermediate source of energy, particularly in automobiles, fuel cells, space heating, electric power generation, a chemical and so on. However, the likelihood of the methanol implementation in these capacities requires a higher level of understanding and knowledge of the oxidation processes. A new kinetic mechanism for methanol oxidation at low pressure has been developed. The proposed model has been validated using three experimental premixed laminar methanol flames. The obtained data infer that the developed mechanism predicts well the concentrations of the major reactants, intermediates, and products at all the studied equivalence ratios. The production rates analysis of selected species allowed the identification of the major formation and depletion pathways. A reaction path analysis showed that the main channels in methanol consumption involved H, OH and O attack and the resulting radicals CH₂OH and CH₃O produced formaldehyde.

Keywords— methanol; oxidation; model; premixed flame; validation

I. INTRODUCTION

Oxidation of methanol has been studied at high temperatures in shock tubes [1-5], jet-stirred reactors [6] and flames [7-9], and in the low-to-medium temperature range in batch reactors [10] flow reactors [11-14], and supercritical water [15-17]. It is well known that the development of detailed chemical kinetic models allow interpretation of the kinetic behavior of the experiments used in their validation. Thus, in order to describe methanol experiments in term of reaction mechanism containing elementary steps, a few detailed models have been proposed and discussed. Westbrook and Dryer [18] developed a mechanism for methanol oxidation, applicable to temperatures in the range 1000-2200 K, pressures of 1-5 atm, and equivalence ratios of 0.05-3.0. This model has been applied in a number of studies on methanol to simulate the results (ignition delay times, flame velocities, and species concentrations) of

many different experiments. However, this work was hampered by a lack of elementary rate constant and reaction path information. Dove and Warnatz [19] proposed a new mechanism containing 15 species and 40 elementary reactions which was used by Pauwels et al [20] to simulate their stoichiometric methanol-air flame data. It was found that the model predicted CO and H₂ concentrations larger than those measured whereas the reverse holds for the CO₂ profiles. As new information on methanol oxidation (new rate constants and a consistent set of thermochemical parameters) became available, the Westbrook and Dryer mechanism was modified by Norton and Dryer [12]. A better agreement with the flow-reactor data has been observed, and the importance of the hydroperoxyl radical (HO₂) to methanol oxidation kinetics has been noticed. A more recent methanol oxidation mechanism was constructed by Egolfopoulos, Du, and Law [21]. The authors have found that their model predicted excellently both the laminar flame speed and atmospheric-pressure flow-reactor data set [22]. However, the ability of the model to predict the Bowman's shock-tube ignition delay measurements has been questioned [3]. Recently, Held and Dryer, using a hierarchical procedure, have developed a detailed comprehensive kinetic model that includes advances in chemical kinetic rate and thermochemical information as well as validation data sources [23]. It was found that this model satisfactorily reproduces measurements from four different types of experiments (static reactors, flow reactors, shock-tubes and laminar flames) over a wide range of temperature, pressure, and equivalence ratio. However, it does not reproduce H and H₂ profiles, in premixed flames, with a good accuracy. Thus, it is observed that despite these extensive efforts, important aspects of methanol chemistry are still unresolved especially at high temperatures.

To gain a more detailed understanding of methanol oxidation in the low pressure, high temperature regime, a detailed chemical kinetic model has been constructed and validated by comparison to data available in the literature.



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II. MODEL DEVELOPMENT PROCEDURE

Base on the H_2 , CO , CH_2O and CH_3OH combustion chemistry, a detailed mechanism for methanol oxidation was hierarchically developed. The reaction submechanisms of each of the above species used here were based on previously published studies. The mechanism was developed by evaluating the importance of each species and reaction step for the chemical processes by sensibility analysis. Unimportant reaction species and steps are judiciously removed.

For each elementary reaction; the overall rate constants proposed in the literature were tested and then their influence on the molar fractions profile of stable and unstable species in the various studied flames was checked. For each elementary reaction, the constant rate giving the best agreement between experimental and modelled profiles for different species was selected. On the other hand, it was found that C_2 submechanism as well as CH and CH_2 (singlet and triplet states) reactions had no significant effects on stable and unstable species concentration profiles. Same trends were reported by several authors [24-26] for methanol combustion over almost all conditions of practical interest. Taking these observations into account, a detailed homogeneous gas-phase kinetic mechanism containing 19 species involved in 115 elementary reactions has been developed for the CH_3OH oxidation.

III. COMPUTATIONAL PROCEDURE

Computations were carried out using the Sandia laminar one-dimensional premixed flame code (PREMIX) [27] of the Chemkin package [28]. The PREMIX code computes concentration profiles for a burner-stabilized premixed laminar flame using the cold mass flow rate through the burner, feed-gas composition, pressure, and an initial guess of the solution profile as input. To compensate for the cooling effect of the flame by the probe and the burner, the Vandooren and Van Tiggelen experimentally determined temperature profile was used as input [7]. The reverse reaction rates were calculated using equilibrium constants and species thermodynamic data taken from the literature [29-32] or theoretically computed.

IV. MECHANISM VALIDATION

Three sets of low-pressure burner-stabilized flat flame data are available in the literature. The set of Vandooren and Van Tiggelen [7], the set of Pauwels, et al [20] and the set of Bradley et al. [34] In this work, comparisons were made with the

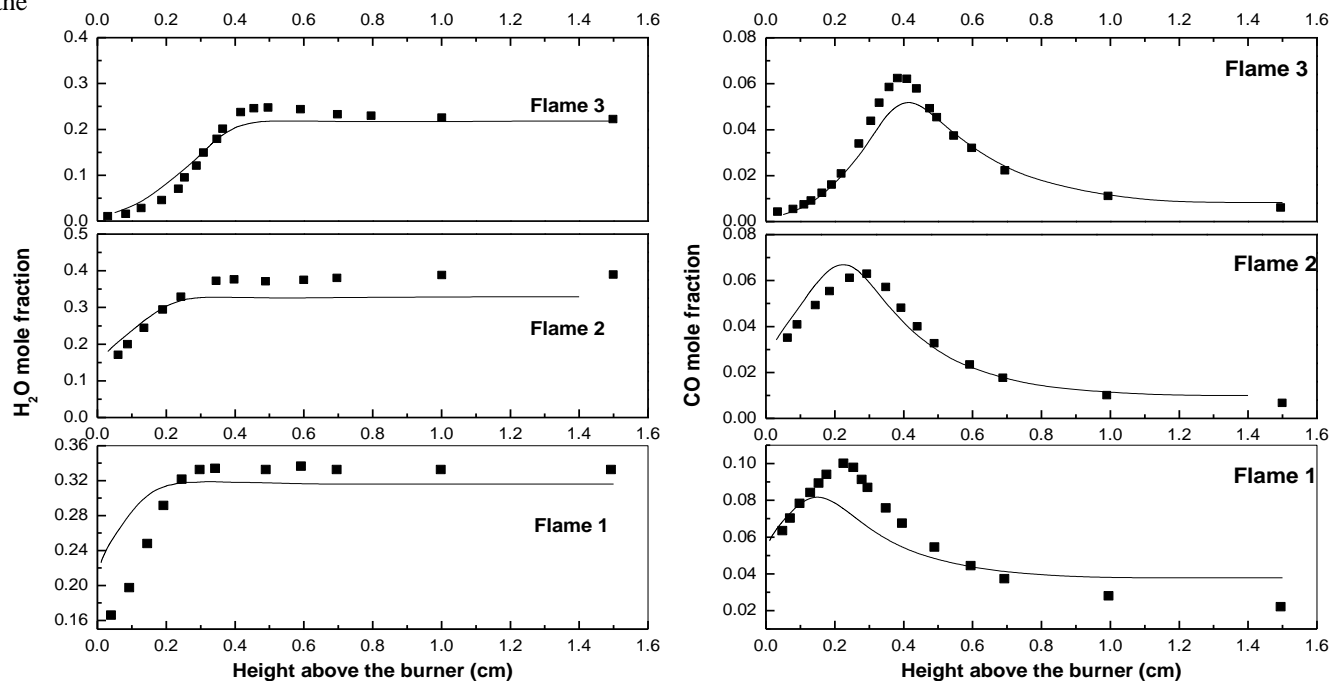
data of Vandooren and Van Tiggelen because of their comprehensive character [23].

In their study, Vandooren and Van Tiggelen [7] used the molecular beam sampling technique, coupled with mass spectrometric detection to measure the concentrations of both stable species and radicals such as H , OH and O . Table 2 lists their three well-studied burner-stabilised laminar premixed flames compositions and operating conditions that the developed model has been compared against.

TABLE I
Initial conditions of laminar lean premixed $CH_3OH/O_2/Ar$ (Flame I),
 CH_3OH/O_2 (Flame II) and $CH_3OH/H_2/O_2$ (Flame III).

	Flame I	Flame II	Flame III
CH_3OH	19.9 %	19.4 %	10.9 %
O_2	33.7 %	80.6 %	85.9 %
Ar	46.4%	-	-
H_2	-	-	3.2 %
Equivalence ratio	0.89	0.36	0.21
Pressure (Torr)	40	40	40
Initial velocity of the fresh gases (cm/s)	43	44	78

As a first step, the discussion will be focused on the ability of the model to correctly predict the mole fraction profiles of the reactants, intermediates and products in the three flames. Representative results for these comparisons are shown in Figures 1 to 5





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Fig 1 Comparison between computed (lines) and experimental (symbols) mole fraction profiles of H₂O and CO for Flames (I, II, III) of Vandooren and Van Tiggelen [7] at T₀ = 298K and P = 0.0526 atm.

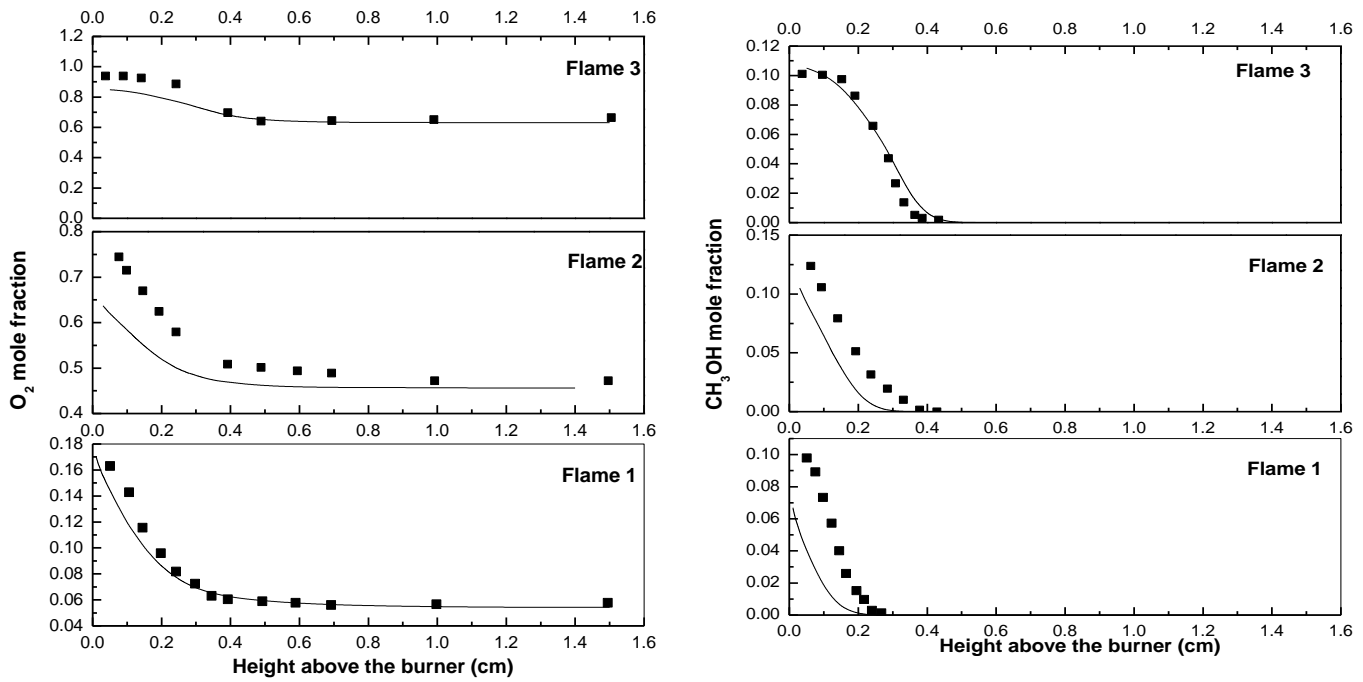


Fig 2 Comparison between computed (lines) and experimental (symbols) mole fraction profiles of O₂ and CH₃OH for Flames (I, II, III) of Vandooren and Van Tiggelen [7] at T₀ = 298K and P = 0.0526 atm.



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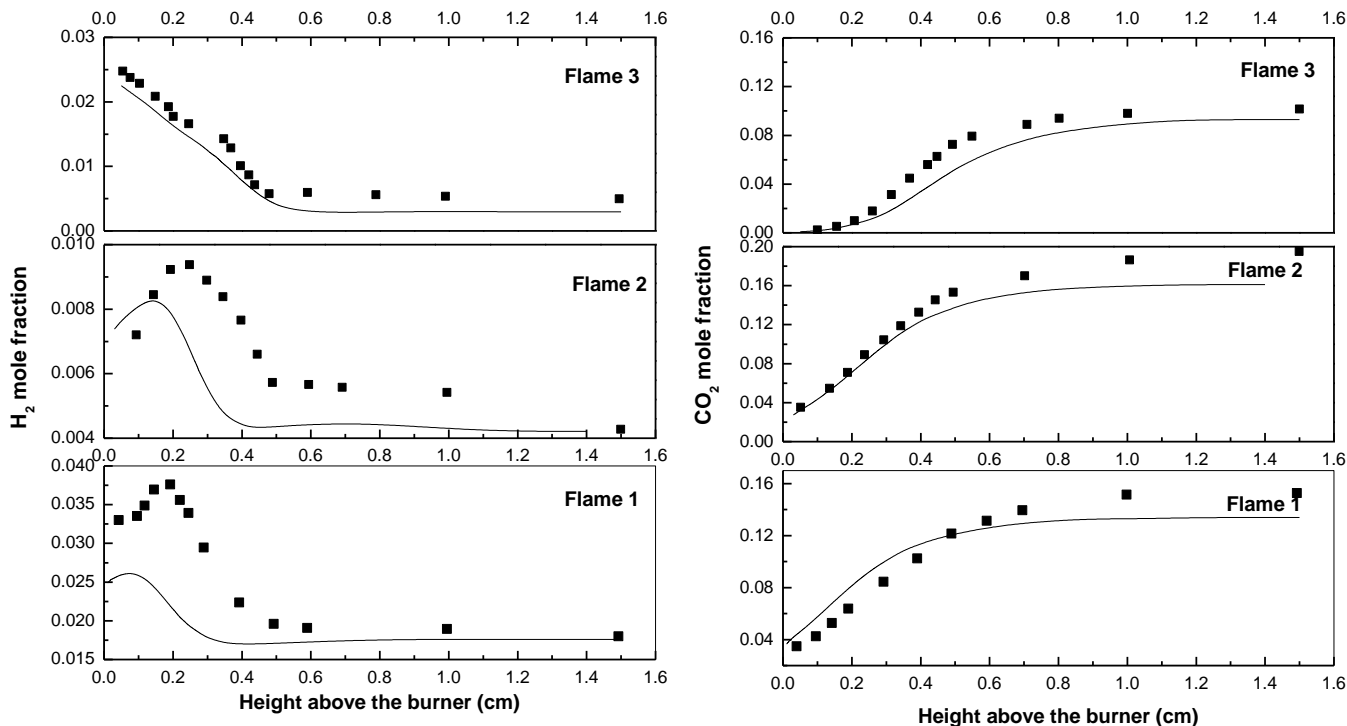


Fig 3 Comparison between computed (lines) and experimental (symbols) mole fraction profiles of H_2 and CO_2 for Flames (I, II, III) of Vandooren and Van Tiggelen [7] at $T_0 = 298K$ and $P = 0.0526$ atm.

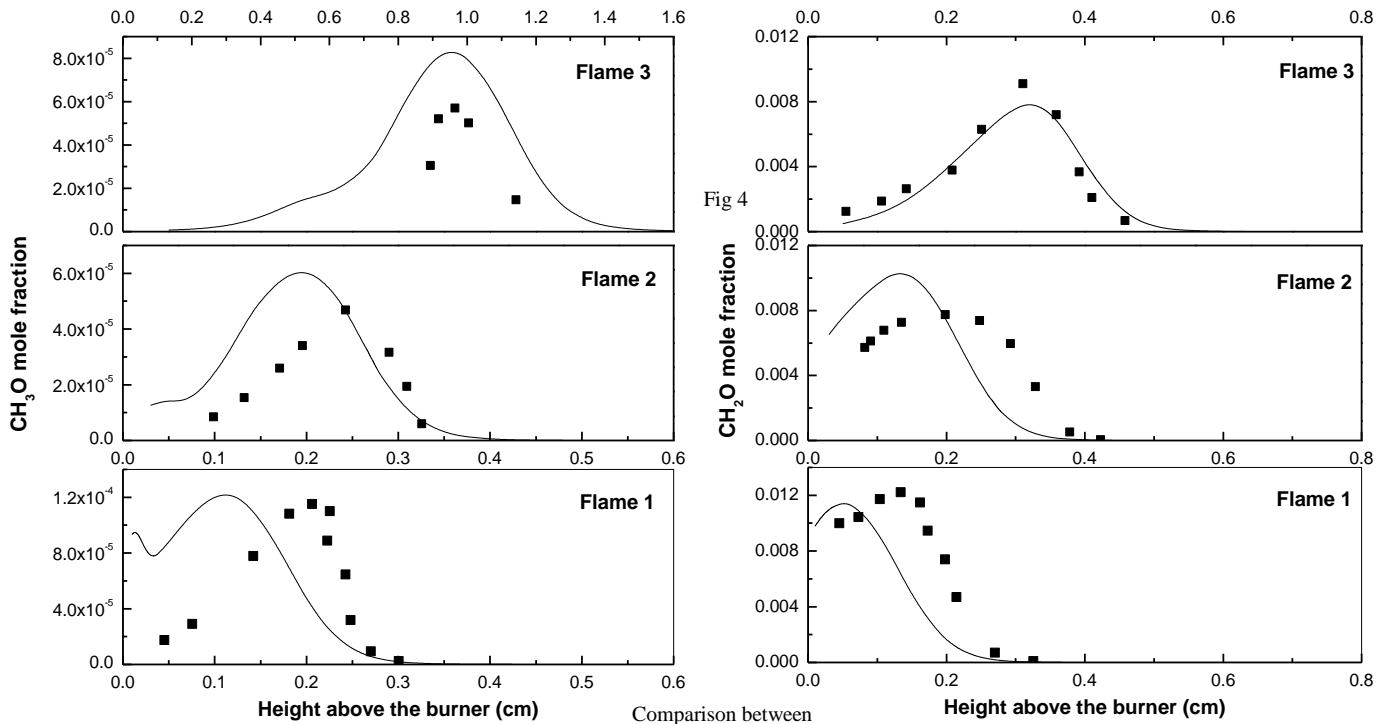
In the case of the lean flame (flame I), it was found that the model matches well the experimental stable species data, with the exception of CH_3OH which was underpredicted near the burner surface (Figures 1-3). This effect may be ascribed to the flame disturbance by the MBMS sampling cone. For unstable species (H , O , OH , CH_2O and $(CH_2OH + CH_3O)$), it can be clearly seen that, in general, the key intermediate species concentration profiles were well reproduced by the reaction model (Figures 4, 5).

In the case of flame II, results showed a very good agreement for all stable species, except for molecular hydrogen (H_2) for which the computed profile was slightly delayed relative to the experimental one and the peak value seemed to be underpredicted (Figures 1-3). Besides, for unstable species, the predicted profiles species concentrations were in excellent agreement with the measured ones except for CH_2O profile which was slightly delayed and overpredicted as compared to the experimentally determined one (Figures 4,5).



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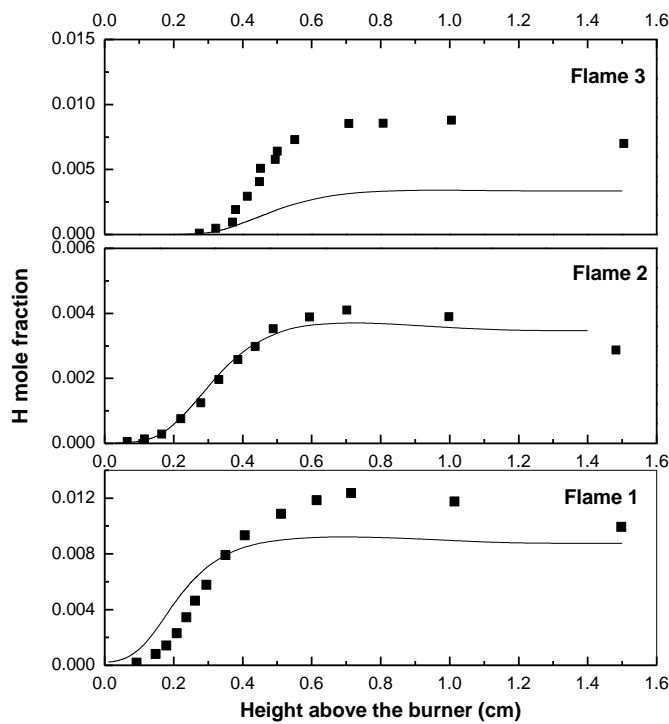
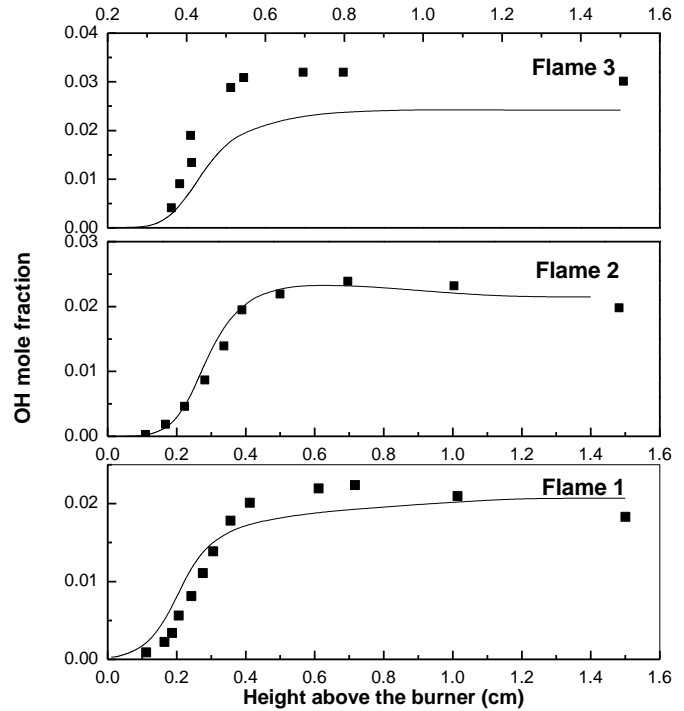
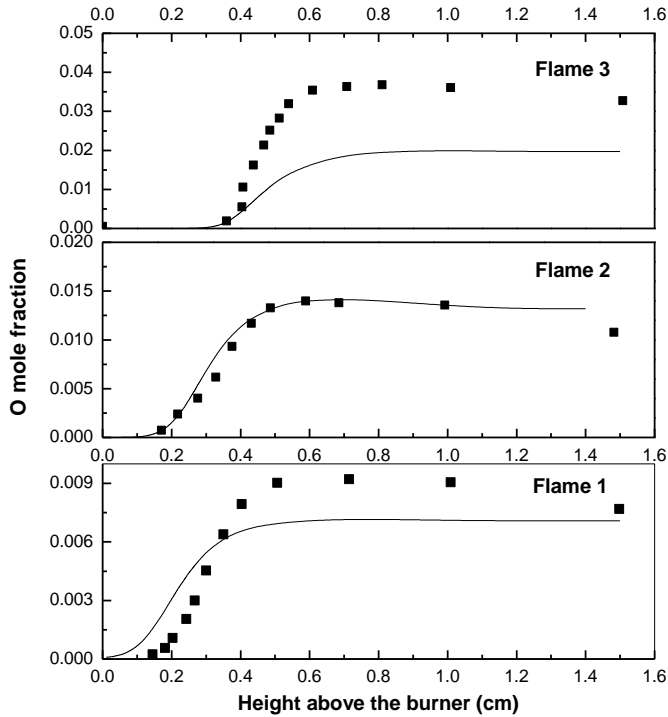
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Fig 5 Comparison between computed (lines) and experimental (symbols) mole fraction profiles of HO, H and O for Flames (I, II, III) of Vandooren and Van Tiggelen [7] at $T_0 = 298\text{K}$ and $P = 0.0526\text{ atm}$.

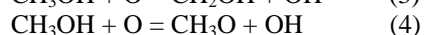
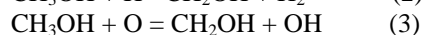
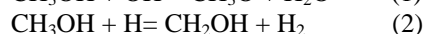
In the case of flame III, for all stable species a very good agreement between computed and experimental results are observed. For the intermediate species, the computed and experimental mole fraction profiles for CH_3O and CH_2O are in very good agreement. Besides, the predicted and measured H, OH and O profile shapes are in good agreement, but the magnitudes of the experimental data are significantly higher than predicted (Figure 5). Same trends were reported by Egolfopoulos and Law [21]. This is probably due to the effect of the addition of H_2 in the initial flame composition.

V REACTION PATHWAYS

The individual contributions of the elementary reactions to the global evolution rates for each species were calculated. Thus, the main reactions relative to specified species analyzed were delineated. In this section, only the main reactions which have an important role in chemicals belonging system C_1 (CH_3OH , CH_2OH , CH_3O , CH_2O) will be presented. H_2/O_2 and CO/CO_2 systems are relatively well known.

V.I. Fuel destruction / CH_3OH

After the initial decomposition of methanol, the major paths consuming fuel is the H, O and OH attack leading to H abstraction, according to:



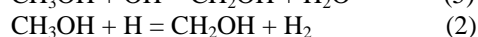
Reactions 3 and 1 dominate in flames II and III while the reaction 2 is the most important in the case of flame I). In addition, all reactions involving CH_3OH consumption produces CH_2OH and its isomer CH_3O .

V.II. Reactions of $\text{CH}_2\text{OH}/\text{CH}_3\text{O}$ and CH_2O

The most important intermediates from initial methanol oxidation are methoxy CH_3O and hydroxymethyl CH_2OH radicals. These intermediates were found to be a very important species in the higher hydrocarbon oxygenates oxidation and pyrolysis.³⁵ Since these two isomers tend to travel different paths.

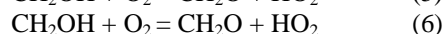
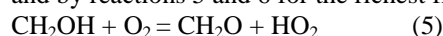
a. CH_2OH reactions

The CH_2OH radical is formed from methanol via the reactions 5, 2 and 3:



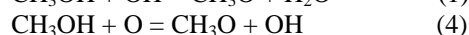
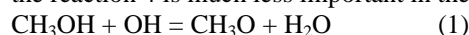
In the case of flame 1, the predominant channel is reaction 2, whereas reaction 3 contributes weakly to CH_2OH production.

While formed, CH_2OH radical leads to the production of formaldehyde, mainly by the reaction 5 for flames (I and II) and by reactions 5 and 6 for the richest flame I:

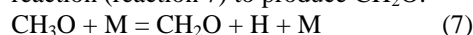


b. CH_3O reactions

The radical CH_3O is mainly formed by methanol attack with OH and O (reactions 1 and 4) for the three flames. However, the reaction 4 is much less important in the case of flames I.

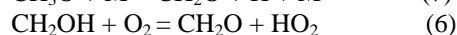
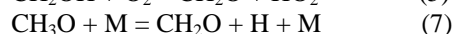
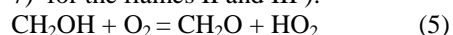


The radical CH_3O is then decomposed via a unimolecular reaction (reaction 7) to produce CH_2O :

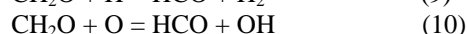
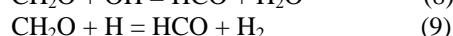
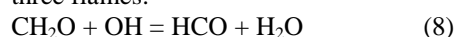


c. CH_2O reactions

Formaldehyde is produced by the bimolecular reaction of CH_2OH with molecular oxygen (reactions 5 and 6) in the case of flame 1, while it is formed either by bimolecular reaction of CH_2OH with molecular oxygen (reaction 5) or by the unimolecular decomposition of the methoxy radical (reaction 7) for the flames II and III):



When formed, the formaldehyde CH_2O reacts with OH, H and O to form formic acid (HCO) via reactions 8, 9, and 10 for the three flames:



The reaction $\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$ is the predominant formaldehyde consumption channel.

VI CONCLUSION

A new detailed CH_3OH oxidation mechanism was developed in a hierarchical manner by assembling selected reaction subsets from existing mechanisms for H_2 , CO , CH_2O , and CH_3OH species. Evaluation of the detailed reaction mechanism has been carried out using the data set of Vandooren and Van Tiggelen because of their comprehensive character. The modeling results show that the developed kinetic scheme displays a good to excellent agreements



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between predictions and measured mole fraction profiles for reactants, products, and intermediates species. Reaction path and analyses allow identification of important kinetic routes and reaction rates of selected species.

Methanol consumption was found to be initiated by hydrogen abstraction with H, OH and O while the resulting radicals CH_2OH and CH_3O were then consumed respectively by reactions $\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$ and $\text{CH}_3\text{O} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M}$ to give formaldehyde.

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